

**Modification of GaN Schottky Barrier Interfaces Probed by
Ballistic-Electron-Emission Microscopy and Spectroscopy**

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Ballistic-electron-emission microscopy (BEEM) and spectroscopy have been used to investigate the properties of Au/GaN interfaces. The effects of in-situ and ex-situ annealing on the starting GaN surface were examined, with the aim of increasing the surprisingly low value of interface electron transmission observed in previous BEEM measurements. BEEM imaging and spectroscopy have demonstrated that much higher, more uniform transmission across the Au/GaN interface can be achieved. However, while methods were identified that increase transmission by more than an order of magnitude, BEEM spectroscopy indicates that annealing can substantially alter the Schottky barrier height. These barrier height changes at moderate temperatures are attributed to vacancy diffusion.

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Devices based on GaN and related group III-nitrides continue to develop, and the need for a more complete understanding of the material and interface properties of GaN has become increasingly important. Many properties of GaN are still not completely understood, and the presence of high defect densities limits the ability of macroscopic probes to extract fundamental electronic properties. The difficulties encountered in growth¹ and surface preparation^{2,3} have been extensively reported. Devices such as high-power amplifiers and ultraviolet photodetectors require high-quality interfaces to be formed to the nitrides, underscoring the need for high-resolution characterization of interface properties.

Ballistic-electron-emission microscopy⁴ (BEEM) was developed from scanning tunneling microscopy⁵ (STM) as a method for applying the high spatial resolution of STM to subsurface characterization. BEEM provides precise measurements of interface barrier height, other features of interface band structure (such as higher conduction-band minima), interface transmission efficiency, and interface heterogeneity.

Because of its high spatial resolution and spectroscopic capabilities, BEEM is a valuable method for characterizing interface quality. Previous BEEM investigations of metal contacts on GaN have shown hot-electron transmission across the metal/semiconductor (M/S) interface to be weak, as much as two orders of magnitude lower than expected for an ideal interface.^{6,7} The difficulty of achieving a clean surface by chemical methods^{2,3} has led to further work involving annealing of the GaN surface both before and after transfer to ultra-high vacuum (UHV) for metal deposition and Schottky contact formation. This letter describes the effects of annealing on both barrier height and interface uniformity of Au/GaN contacts, as determined by BEEM imaging and spectroscopy. These results illustrate the high degree of control over metal/GaN interface barrier height obtainable by thermal processing.

Most previous BEEM measurements on GaN yielded no detectable current. However, successful results were achieved on material grown at Rockwell Science Center, as described elsewhere in more detail.⁶ The n-type GaN was grown by metal-organic chemical vapor deposition on a (0001)-oriented sapphire substrate. After growth, the GaN wafers underwent a rapid thermal anneal (RTA) in N₂ for 90 seconds in order to process Al ohmic contacts. Some results on material that did not receive this RTA will also be discussed. For BEEM experiments, wafers were diced into 4 mm squares and were transferred into a nitrogen-purged glove-box for cleaning. Samples were spin-etched in this glove-box and directly transferred into the load-lock attached to the UHV evaporation chamber.

Annealing of GaN was performed either in N₂ or in UHV prior to Au deposition. Annealing in N₂ was done in the sample preparation glove-box. The GaN was then transferred directly into vacuum for Au deposition. Alternatively, annealing was done after transfer into the Au evaporation chamber. The sample was mounted to a resistively heated holder, and temperature was measured using a thermocouple. The sample required approximately 2 min to cool to less than 100°C, after which it was transferred to a second sample holder for Au evaporation. BEEM measurements were performed at room temperature in a nitrogen glove-box. Usually, many spectra from a given sample were averaged together in order to decrease the noise level in the data. Tunnel current was 2 nA unless otherwise indicated.

Previous BEEM results⁶ were for GaN surfaces that had been spin-etched using 1:10 HCl:ethanol, followed by direct sample transfer from the glove-box into vacuum for Au evaporation. Figure 1 illustrates a typical BEEM spectrum for these samples. Sub-picoampere currents were usually observed, and the spatial variation of the current was

substantial. SB height was uniform, however, and a value of 1.06 ± 0.02 eV was reproducible. Spectra displayed an unexpected shape consistent with the presence of a second conduction band minimum about 0.2 eV above the lowest minimum, which was also reproducible. The second threshold is required to obtain a good fit to the data, and it can be more clearly seen in less heavily averaged spectra.⁷ Occasional high-current areas were also observed, similar to those previously reported⁸ and correlated with GaN defects. These were infrequent, and were excluded from the analysis presented here.

Although other chemical treatments were investigated, none resulted in significant improvement in interface transmission. Boiling aqua regia has been used by other groups and has been found to be effective in GaN surface cleaning.^{9,10} This method was evaluated by aqua regia cleaning in air prior to the glove-box HCl spin-etch procedure. This procedure did not lead to a large improvement in interface transmission. In fact, BEEM collector current, measured at the same value of $V - V_b$, is nearly the same as for HCl cleaning alone.

The effect of annealing of the GaN was much more pronounced. Samples were spin-etched with HCl/ethanol prior to annealing. Annealing was done in UHV or in N_2 prior to Au contact deposition, with similar results for both procedures. For lower annealing temperatures ($< 350^\circ\text{C}$ for up to 30 min), BEEM transmission increased substantially. Figure 2a is a spectrum for Au/GaN where the GaN was annealed in UHV at 340°C for 15 min. SB height remained relatively high, although reduced relative to unannealed samples. For annealing between 350°C and 600°C , a further decrease in SB height resulted, with lower barrier heights for higher annealing temperatures. Figure 2b shows a BEEM spectrum obtained on a Au(8nm)/GaN sample for which the GaN had been annealed at 580°C . Here, the SB height has been reduced to about 0.70 eV.

Increased noise in the spectrum is due to the low barrier height, producing high leakage current and lower signal-to-noise ratio for current measurement.

The lowering of SB height upon annealing was not a reversible process. Subsequent air exposure and chemical cleaning of an annealed wafer chip, onto which new Au contacts were evaporated, produced samples that displayed the same lowered threshold as that for the initial annealed sample.

BEEM interface transmission also increased further for these higher annealing temperatures. Current for Fig. 2b is more than an order of magnitude higher than in Fig. 1. At equivalent energies above the SB, for example at $V-V_b=0.5$ V, current is still nearly a factor of ten higher than for chemically prepared GaN. Similar results were observed for annealing in N_2 prior to Au deposition.

Imaging on these annealed samples showed uniformly high transmission, except in areas of apparent contamination. Figure 3 shows an STM/BEEM image pair from the same sample as that from which the spectrum in Fig. 2b was obtained. Except for an area to the left where transmission is nearly zero, current is fairly uniform at an average value of about 5 pA, in good agreement with the value obtained from Fig. 2b.

This increase in interface transmission by an order of magnitude is substantial and reproducible. Previous work has evaluated the effectiveness of various surface cleaning procedures for GaN,^{3,11} and conventional measurements of the Au/GaN SB height have been found to depend critically on the GaN surface preparation.^{10,12,13,14} It has been found that in-situ thermal cleaning is more effective than chemical treatments, although none of these procedures produces a contamination-free surface.³ Nitrogen ion bombardment can produce a clean surface¹¹, although at the expense of surface damage.

Most work on the effects of annealing on M/S contact properties has been for purposes of ohmic contact formation, in which the annealing occurs after metal deposition;¹⁵ the effect of prior annealing on SB interfaces has been less thoroughly investigated. The present BEEM results show that Au/GaN interface transmission is much larger and much more uniform for thermal surface treatments than for chemical cleaning, although still somewhat lower than expected for an ideal interface.

The cause of the large change in Schottky barrier height with annealing temperature was investigated further. Preliminary BEEM results for GaN that did not undergo the initial RTA reveal behavior that is quite different. As-grown material produced Schottky contacts for which the zero-bias leakage current was too large for BEEM data acquisition, although I-V measurements yielded a barrier height of ~ 0.60 eV. Annealing at temperatures less than 300°C did not result in measurable improvement in leakage. Annealing at higher temperatures, however, produced spectra with low enough noise for BEEM measurements. In this case, annealing at 400°C increased barrier height to 0.72 eV. These results on as-grown GaN will be presented in more detail in a future publication.

Bermudez et al.¹¹ studied the change in surface band bending with annealing, both for as-grown GaN samples and for ion-bombarded samples. In that work, it was proposed that excess near-surface N vacancies in as-grown material, and excess near-surface Ga vacancies in ion-bombarded material, were responsible for the large difference in band bending for these two cases. In both those XPS measurements and these experiments, annealing at temperatures up to 600°C caused the upward band bending to stabilize at a common value of about 0.7 eV. Although those results were for the bare GaN surface, similar behavior is observed here for the barrier heights of GaN Schottky contacts. The results from ref. 11 for initially large (~ 1.1 eV) band bending

upon ion bombardment correspond to the large Schottky barrier height seen here for GaN which underwent an initial RTA in nitrogen before further processing. This suggests that the RTA creates an excess of near-surface Ga vacancies, due to loss of surface Ga at high temperatures. While short anneals allow relatively little diffusion to occur, lower-temperature, longer-duration annealing tends to restore thermodynamic equilibrium¹⁶ for both as-grown and RTA-processed GaN, and to move the SB height to a common value.

In conclusion, the effects of annealing on Au/GaN SB structures have been investigated using BEEM spectroscopy and imaging, with the goal of increasing transmission across this interface. Annealing at moderate temperatures yields an increase in interface transmission of about an order of magnitude compared with other samples, although transmission is still lower than expected. Higher annealing temperatures cause a substantial change in SB height, the direction of which depends on previous thermal processing. High-temperature rapid thermal annealing in nitrogen before contact formation produces a large increase in SB height compared with that on as-grown GaN, with a measured change of nearly 0.5 eV. These barrier height changes are interpreted in terms of creation of vacancies or their diffusion toward the GaN surface.

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Figure Captions

- FIG. 1. BEEM spectrum for Au(6nm)/GaN, for which the GaN was prepared using HCl:ethanol in a nitrogen glove-box. Also shown is a two-threshold fit to the data.
- FIG. 2. BEEM spectra for two different Au(8nm)/GaN samples. a) Spectrum for a sample annealed in UHV at 340°C for 15 min. Current is considerably enhanced relative to the spectra in Fig. 1. b) Spectrum for a sample annealed at 580°C. Here transmission is increased further, and barrier height is substantially decreased.
- FIG. 3. STM / BEEM image pair for Au/GaN annealed at 580°C. Imaged area is 196 x 110 nm. a) STM image obtained at a tunnel voltage of 0.5 V and a current of 1 nA. Grey scale covers a 5.3 nm height range. b) BEEM image obtained at a tunnel voltage of 1.6 V and a current of 2 nA. Average BEEM current in the light areas is 5 pA, and the dark areas correspond to zero measured current.

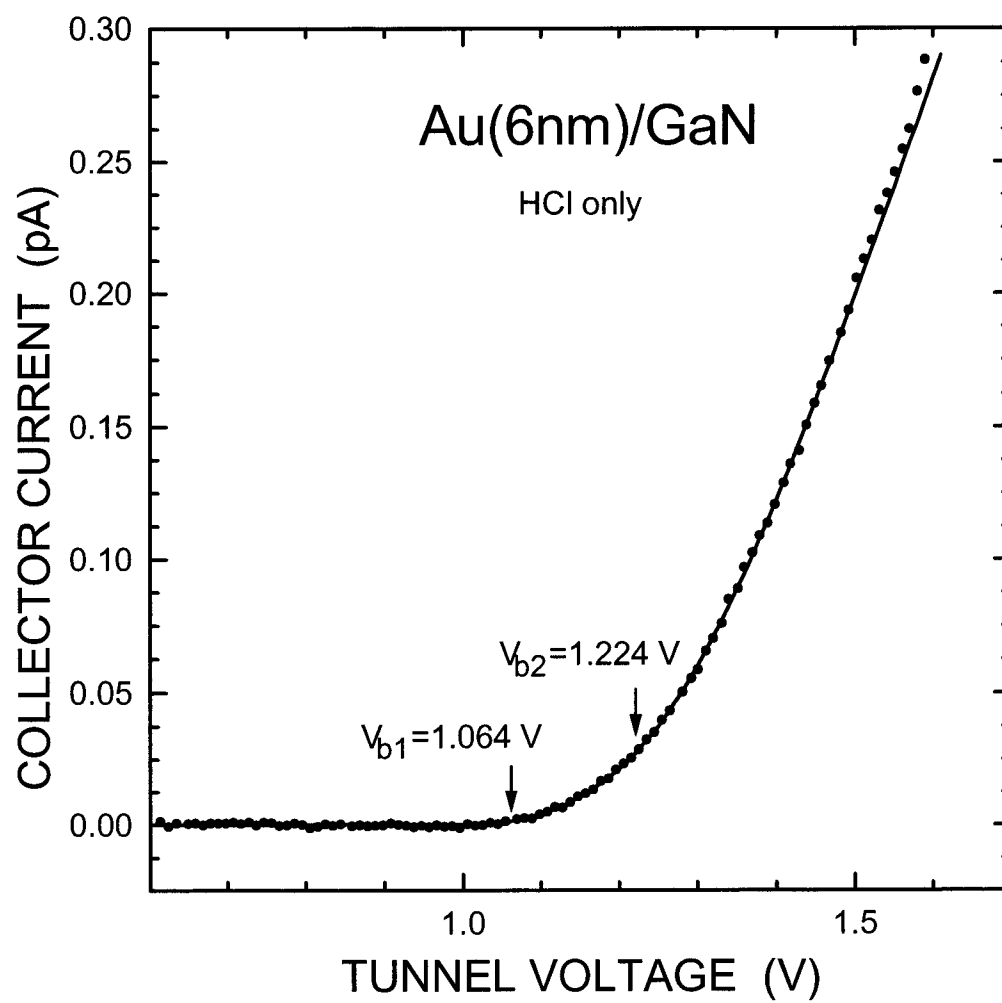


Figure 1
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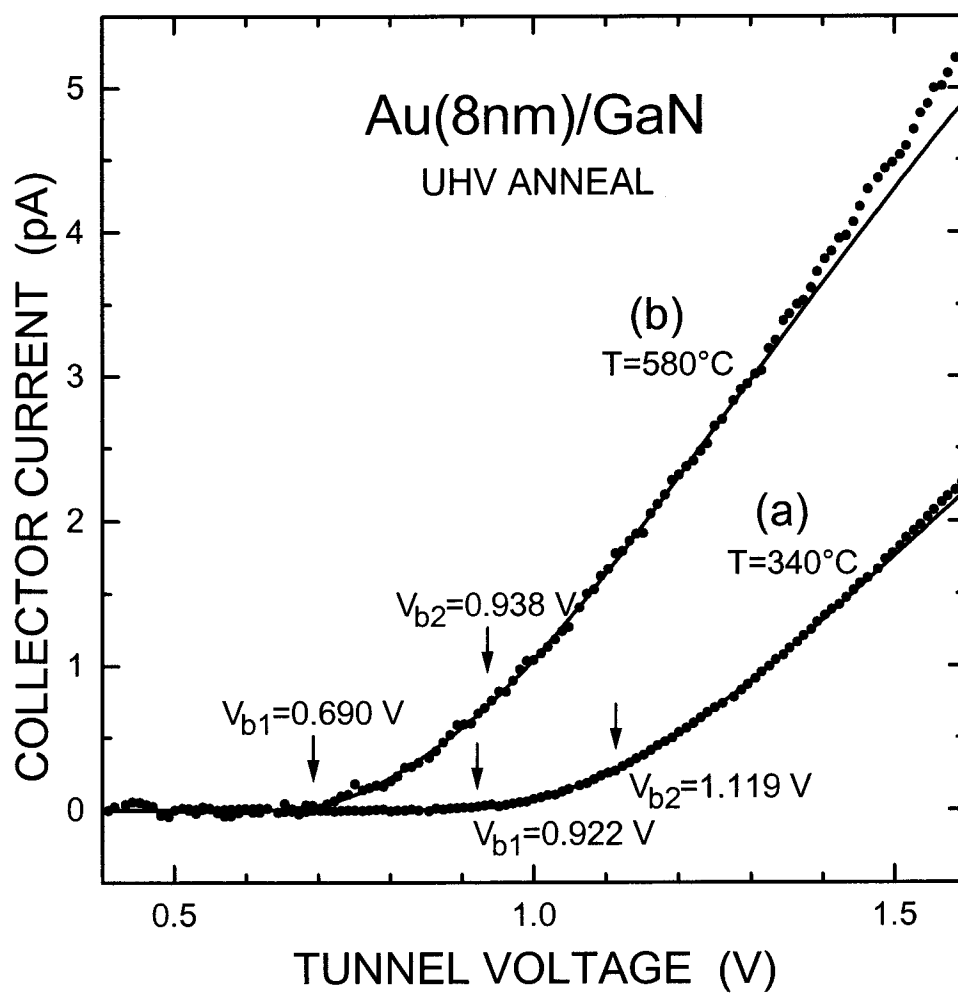


Figure 2
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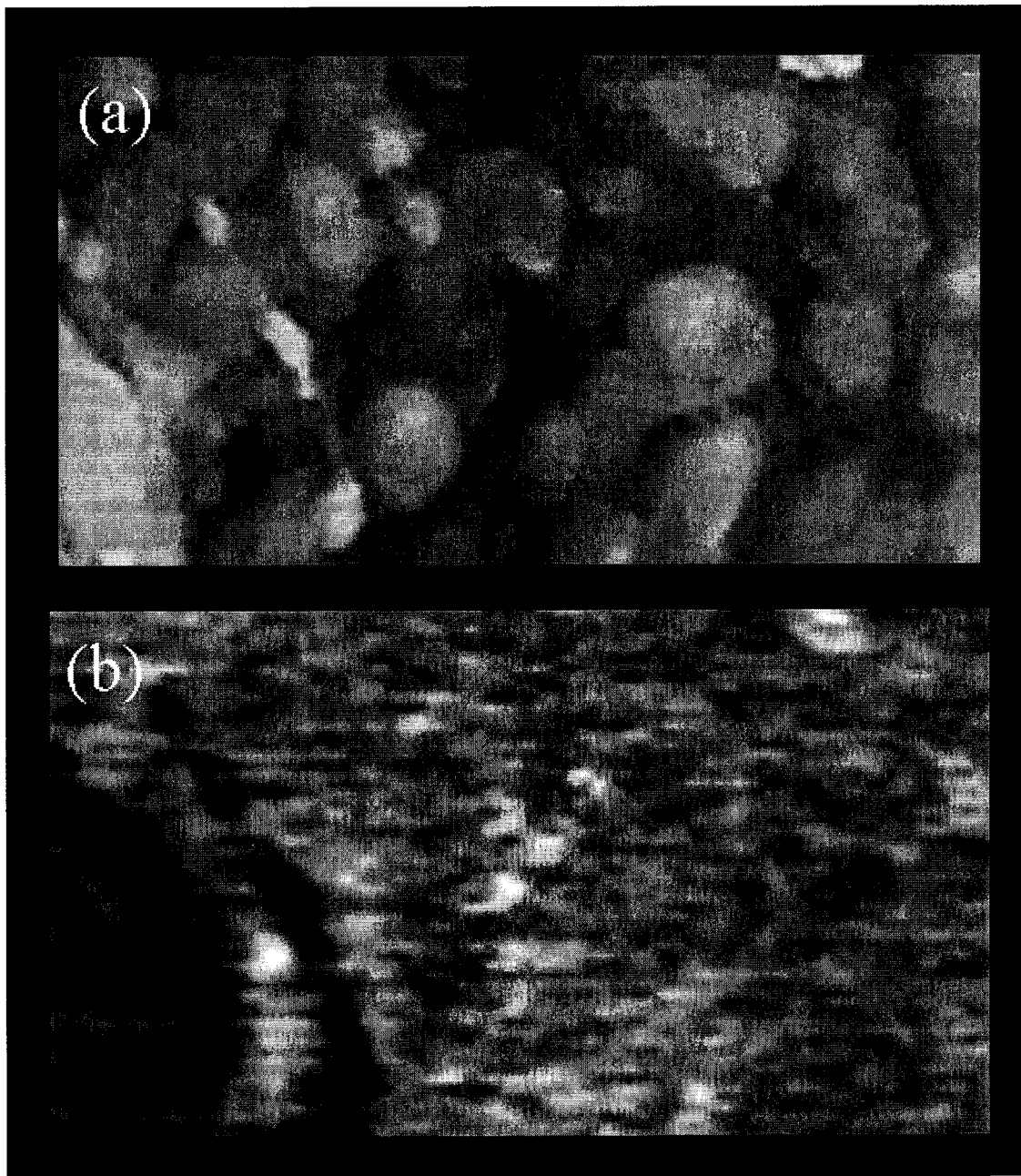


Figure 3
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